Chemistry of Heterocyclic Compounds, Vol. 41, No. 10, 2005

CYCLOTRANSFORMATION OF AZINIUM SALTS INTO HYDROGENATED CYCLIC ALKYLAMINO KETONES

V. I. Terenin and A. S. Ivanov

A study was carried out on the nucleophilic cyclotransformation of pyrrolo[1,2-a]pyrazinium salts and isoquinolinium salts containing a methyl group in the α-position. A method for the preparation of alkylaminotetrahydroindolizinones and tetralones was proposed.

Keywords: isoquinoline, pyrrolo[1,2-*a*]pyrazine, 5,6,7,8-tetrahydroindolizinone, α-tetralone, nucleophilic rearrangement.

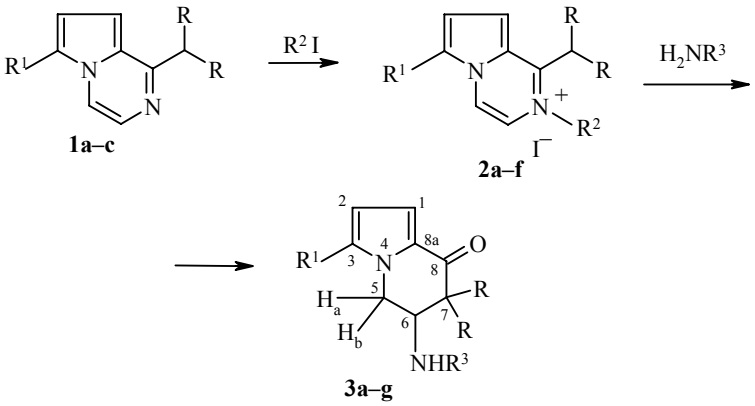
The isomerizational recyclization of azinium salts by the action of nucleophiles known as the Kost–Sagitullin rearrangement involves the exchange of the exocyclic α-carbon atom by a ring nitrogen atom [1]. Heterocycles undergoing cyclotransformation through the ANRORC mechanism form either aromatic or conjugated cyclic structures [2]. The exocyclic carbon atom must have at least two hydrogen atoms required for consecutive reduction of aromaticity of the transformation products, which are either carbocycles or heterocycles. In previous work, we have shown that pyrrolo[1,2-*a*]pyrazinium alkyl iodides containing methylene group at position 1 are converted by the action of alcoholic alkylamines into 8-alkylaminoindolizines [3], while isoquinolinium alkyl iodides are converted to 1-alkylaminonaphthalenes [4]. The nucleophilic transformation of azacycles containing an α-methine substituent was not examined due to the above reasons. We are the first to discover the capacity of aromatic heterocyclic compounds **2a-f** and **5a-c** containing a methine substituent at the α-position relative to the cyclic nitrogen atom to undergo a previously unreported cyclotransformation to give hydrogenated cyclic alkylamino ketones **3a-g** and **6a-c,** including spirocyclic compounds.

A comparative analysis of the ^{1}H NMR spectra of nitrogenous bases **1a-c, 4a,b** and cyclotransformation products **3a-g** and **6a-d** revealed clear structural features of these compounds. The disappearance of the signals of the protons of the pyrazine system in the case of starting **1a-c** and the pyridine system in the case of **3a** and **3b** as well as of the methine hydrogen atom and the appearance of signals of diastereotopic protons in the resonance range of aliphatic groups protons indicates recyclization of the starting azacycles. The structures of **3b** and **6b** were also supported by ^{13}C NMR spectroscopy. The IR spectra of the products show C=O and NH group stretching bands.

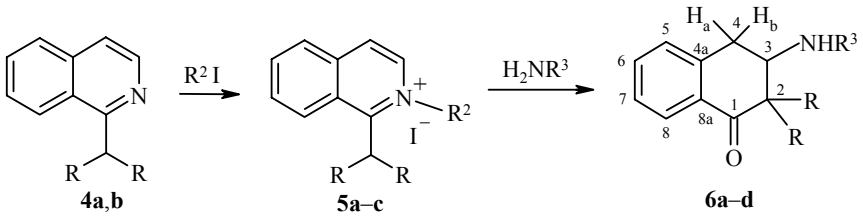
Variation in the reaction temperature and duration in the reaction of alcoholic solutions of alkylamines with pyrrolo[1,2-*a*]pyrazinium salts **2** hardly affects the yield of the recyclization products. The reactions with isoquinolinium salts **5** proceed somewhat differently. The ratio of the products of dealkylation **4a** and recyclization **6a** in the case of the reaction of 1-isopropyl-2-methylisoquinolinium iodide (**5a**) with ethanolic

---

M. V. Lomonosov Moscow State University, 119899 Moscow, Russia; e-mail: vter@org.chem.msu.ru.
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1551-1557, October, 2005. Original article submitted March 16, 2005.



Com-pound	R	R^1	R^2	Com-pound	R	R^1	R^3
1a	Me	H		**3a**	Me	H	Me
1b	Me	Me		**3b**	Me	H	Et
1c	R+R = $(CH_2)_4$	H		**3c**	Me	H	i-Pr
2a	Me	H	Me	**3d**	Me	Me	Me
2b	Me	H	Et	**3e**	Me	Me	Et
2c	Me	Me	Me	**3f**	R+R = $(CH_2)_4$	H	Me
2d	Me	Me	Et	**3g**	R+R = $(CH_2)_4$	H	Et
2e	R+R = $(CH_2)_4$	H	Me				
2f	R+R = $(CH_2)_4$	H	Et				



Com-pound	R	R^2	Com-pound	R	R^3
4a	Me		**6a**	Me	Me
4b	R+R = $(CH_2)_5$		**6b**	Me	Et
5a	Me	Me	**6c**	Me	*i*-Pr
5b	Me	Et	**6d**	R+R = $(CH_2)_5$	Me
5c	R+R = $(CH_2)_5$	Me			

solution of methylamine at 140 and 160°C is 1:2 and 5:1, respectively. The rates of the cyclotransformation and dealkylation are probably similar at 140°C. The rate of the reaction leading to 1-isopropylisoquinoline (**4a**) at 160°C is greater than the rate of the competing recyclization reaction. In the reaction of 1-cyclohexyl-2-methylisoquinolinium iodide (**5c**) with ethanolic solution of methylamine, it was found useful to carry out the reaction at a lower temperature (120°C). This procedure probably takes advantage of the greater steric hindrance produced by the cyclohexyl ring in comparison to the isopropyl group. Nevertheless, the yield of spirocyclic product **5c** remains low.

A study of the transamination of starting pyrrolo[1,2-*a*]pyrazinium alkyl iodides **2** and isoquinolinium alkyl iodides **5** showed the feasibility of the complete exchange of the alkylamine fragment at $C_{(6)}$ in the resultant tetrahydroindolizinone derivatives **3** and at $C_{(3)}$ in tetralones **6**. When $R^2 \neq$ Me at the nitrogen atom in the starting azinium salt and $R^3 \neq$ Me in the alkylamine, the yields of the corresponding recyclization products

are reduced and the products of the dealkylation of the starting salts to give nitrogenous bases are enhanced. This result is likely related to the steric hindrance of the bulky alkyl substituents in the starting salts and in the reagent in the attack of the nucleophile at $C_{(1)}$ in the starting heterocycle.

This newly discovered reaction proceeds through the following scheme. Attack of the nucleophile at α-carbon atom $C_{(3)}$ (pathway A) or $C_{(1)}$ (pathway B) in the case of a quaternary nitrogen atom leads to opening of the heterocycle and formation of intermediates **A1**,**3**. Attack of the enamine fragment on the imine carbon of intermediates **B1-3** leads to formation of cyclic imines **C1-3**, which are then hydrolyzed to give hydrogenated cyclic alkylamino ketones **D1**,**2**. Since the α-methine group contains only one hydrogen atom, aromatization is impossible and recyclization ends with formation of the hydrogenated product. We should note that in the reaction of the 1-isopropylpyrrolo[1,2-*a*]pyrazinium salt and ethanolic solution of isopropylamine, in addition to 6-isopropylaminoindolizinone (**3c**), trace amounts of ketone **D2** are formed as a consequence of reaction through pathway B. Support for the scheme proposed below, we should add that a small amount of a mixture of imines **C2** and **C1** (minor product) was isolated in the reaction of 1-isopropylpyrrolo[1,2-*a*]pyrazinium methyl

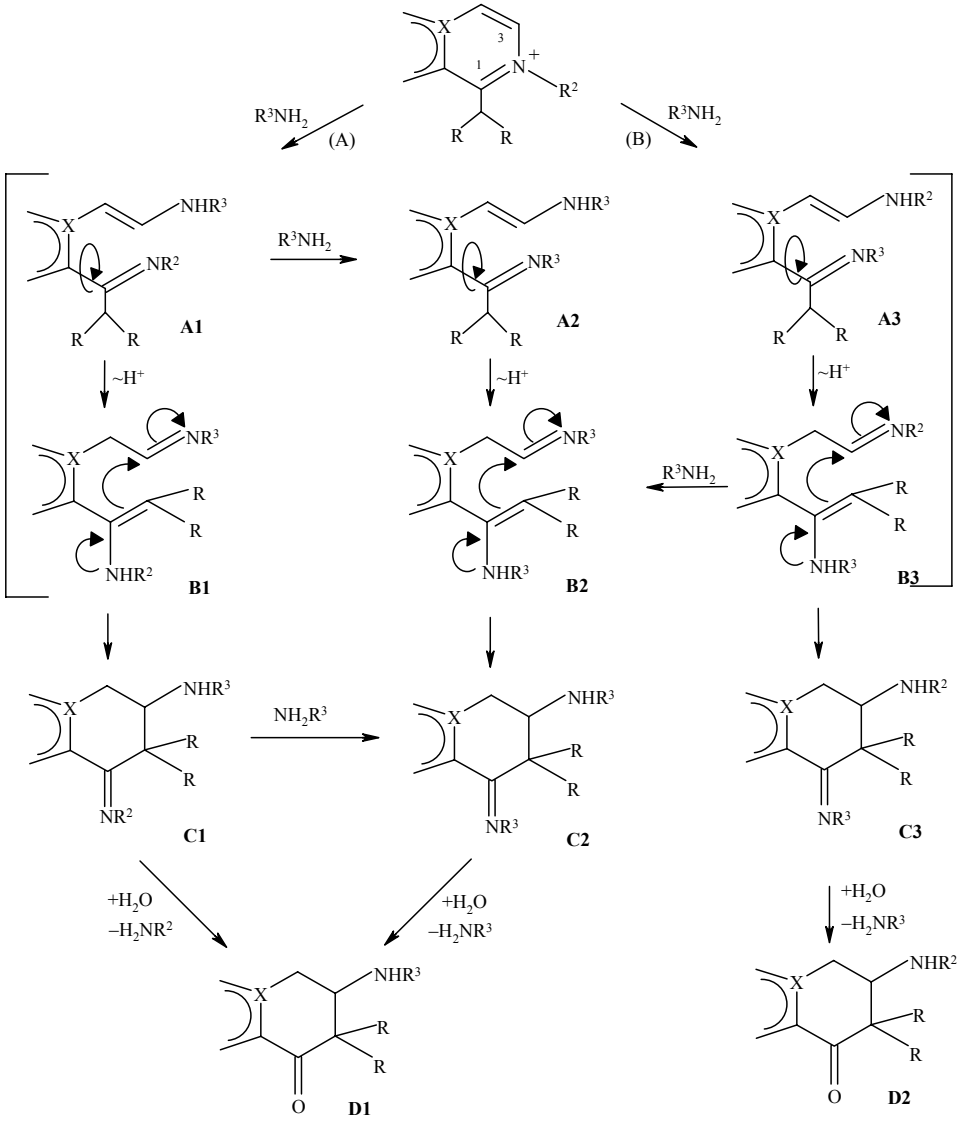


TABLE 1. Yields of Recyclization and Dealkylation Products

Starting salt	Yield of products, %			
	Methylamine		Ethylamine	
	recyclization	dealkylation	recyclization	dealkylation
2a	34 35*	15 19*	23	17
2b	30	15	25	18
2c	43 44* 43*[2]	10 12* 10*[2]	30	14
2d	40	15	26	24
2e	29	33	20	43
2f	27	37	24	37
5a	40 35* 8*[2]	20 35* 51*[2]	25	33
5b	18	50	20	25
5c	7*	62*	—	—

* Reaction was carried out at 120°C.
*[2] Reaction was carried out at 160°C.

iodide (**2a**) with ethanolic solution of ethylamine and these imines were detected by ^{1}H NMR spectroscopy. In addition to signals for the pyrrole ring protons, signals were found for the protons of two ethyl groups of imine **C2**, while signals for protons of the methylimine and ethylamino groups were detected for the minor product, **C1** (see Experimental). In all likelihood, the initial attack of the nucleophile occurs at $C_{(3)}$ along with attack at α-carbon atom $C_{(1)}$. However, we cannot evaluate the preference for nucleophilic attack at $C_{(1)}$ or $C_{(3)}$ of the azine ring using the ratio of integral intensities of the protons in the abovementioned spectrum of imines **C1** and **C2** since intermediates **A1** and **B3** and imine **C1** in the case of a large excess of alkylamine should undergo transamination.

Such ring transformation is undoubtedly general in nature since it has been demonstrated for the pyrrolo[1,2-*a*]pyrazine and isoquinoline systems and is a new method for the preparation of tetrahydroindolizinones and tetralones, including spirocyclic products **3f,e,** and **6c,** containing an alkylamino group.

EXPERIMENTAL

The ^{1}H NMR spectra were taken on Varian VXR-400 and Bruker Ultra Shield spectrometers (400 MHz) in $CDCl_3$ at 28°C with TMS as the internal standard. The mass spectra were taken on a Kratos MS-90 mass spectrometer at 70 eV ionization voltage. The IR spectra were taken on a UR-20 spectrometer in CCl_4. The reaction course and purity of the products were checked by thin-layer chromatography on Alufol plates using benzene and 1:1 benzene–ethyl acetate as eluents with development by iodine vapor and ethanolic ninhydrin.

Samples of starting pyrrolo[1,2-*a*]pyrazines **1a-c** were prepared by our previous procedure [5], while isoquinolines **4a**,**b** were obtained according to the classical Bischler–Napieralski method [6] with subsequent aromatization over palladium black.

Preparation of Salts 2a-f and 5a-c (General Method). A mixture of nitrogenous base **1a-c, 4a,b** (3 mmol) and methyl iodide or ethyl iodide (3.5-4 ml) was heated for 2-3 h in a sealed ampule at 70-80°C until the reaction mixture separated into two layers. The upper oily layer was separated and crystallized upon ice

cooling. The crystals were washed several times with cold acetone. The yield of **2a** was 76%; mp 160-161°C. The yield of **2b** was 65%; mp 82-84°C. The yield of **2c** was 72%; mp 163-165°C. The yield of **2d** was 62%; mp 84-86°C. The yield of **2e** was 68%; mp 160-162°C. The yield of **2f** was 52%; mp 123-124°C. The yield of **5a** was 80%; mp 240-241°C. The yield of **5b** was 75%; mp 80-82°C. The yield of **5c** was 45%; mp 171-172°C.

Preparation of Recyclization Products 3a-f and 6a-c (General Procedure). A mixture of quaternary salt **2a-f** or **5a-c** (1 mmol) and 40% ethanolic alkylamine (4-5 ml) was heated in a sealed tube for 6-8 h at 140°C. The solvent was removed in vacuum. The recyclization product was isolated by chromatography on a neutral alumina column (Brockmann activity II) with elution using benzene and subsequent increase in polarity to 1:1 benzene–ethyl acetate.

^{1}H NMR Spectrum of Imine Mixture. A. C2 (6-Ethylamino-8-ethylimino-7,7-dimethyl-5,6,7,8-tetrahydroindolizine), δ, ppm, (*J*, Hz): 1.08 (3H, t, *J* = 7.6, 6-NHCH$_2$<u>CH$_3$</u>); 1.21, 1.23 (both 3H, both s, 7-(CH$_3$)$_a$, 7-(CH$_3$)$_b$); 1.35 (3H, t, *J* = 7.4, 8-NCH$_2$<u>CH$_3$</u>); 2.62, 2.79 (both 1H, both dq, *J* = 7.4, *J* = 11.5, 6-NHC<u>H$_a$H$_b$</u>CH$_3$); 2.88 (1H, dd, J_{65b} = 4.2, J_{65a} = 5.7, H-6); 3.61 (2H, m, 8-NC<u>H$_a$H$_b$</u>CH$_3$); 3.97 (1H, dd, J_{5a5b} = 12.0, J_{5a6} = 5.7, H$_a$-5); 4.20 (1H, dd, J_{5b5a} = 12.0, J_{5b6} = 4.2, H$_b$-5); 6.27 (1H, dd, *J* = 3.7, J_{21} = 2.4, H-2); 6.60 (1H, dd, J_{12} = 2.4, *J* = 1.1, H-1); 6.69 (1H, m, H-3).

B. C1 (Minor Component) (6-Ethylamino-7,7-dimethyl-8-methylimino-5,6,7,8-tetrahydro-indolizine), δ, ppm, (*J*, Hz): 1.09 (3H, t, *J* = 7.4, 6-NHCH$_3$<u>CH$_3$</u>); 1.21, 1.23 (both 3H, both s, 7-(CH$_3$)$_a$, 7-(CH$_3$)$_b$); 2.63, 2.79 (both 1H, both dq, *J* = 7.4, *J* = 11.4, 6-NHC<u>H$_a$H$_b$</u>CH$_3$); 2.87 (1H, dd, J_{65b} = 4.2, J_{65a} = 5.7, H-6); 3.45 (3H, s, 8-NCH$_3$); 4.03 (1H, dd, J_{5a5b} = 12.0, J_{5a6} = 5.7, Ha-5); 4.22 (1H, dd, J_{5b5a} = 12.0, J_{5b6} = 4.2, H$_b$-5); 6.30 (1H, dd, *J* = 3.7, *J* = 2.4, H-2); 6.72 (2H, m, H-1, H-3).

7,7-Dimethyl-6-methylamino-5,6,7,8-tetrahydroindolizinone (3a). IR spectrum, ν, cm^{-1}: 3340 (NH), 1653 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.21, 1.31 (both 3H, both s, 7-(CH$_3$)$_a$, 7-(CH$_3$)$_b$); 2.51 (3H, s, 6-NH<u>CH$_3$</u>); 2.96 (1H, dd, J_{65a} = 6.9, J_{65b} = 3.8, H-6); 4.05 (1H, dd, J_{5a5b} = 12.9, J_{5a6} = 6.9, H$_a$-5); 4.32 (1H, dd, J_{5b5a} = 12.9, J_{5b6} = 3.8, H$_b$-5); 6.26 (1H, dd, J_{21} = 4.1, J_{23} = 2.2, H-2); 6.81 (1H, dd, J_{32} = 2.2, J_{31} = 1.5, H-3); 6.98 (1H, dd, J_{12} = 4.1, J_{13} = 1.5, H-1). Mass spectrum, *m/z* (I_{rel}, %): 192 [M]$^+$ (18), 149 [M - CH(CH$_3$)$_2$]$^+$ (27), 107 [M - C(CH$_3$)$_2$CHNHCH$_3$]$^+$ (53), 98 [M - C$_5$H$_3$NO]$^+$ (100). Found, %: C 68.68; H 8.11; N 14.40. C$_{11}$H$_{16}$N$_2$O. Calculated, %: C 68.72; H 8.3; N 14.57.

6-Ethylamino-7,7-dimethyl-5,6,7,8-tetrahydroindolizinone (3b). IR spectrum, ν, cm^{-1}: 3340 (NH), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.08 (3H, t, *J* = 7.1, 6-NHCH$_2$<u>CH$_3$</u>); 1.17, 1.28 (both 3H, both s, 7-(CH$_3$)$_a$, 7-(CH$_3$)$_b$); 2.62, 2.81 (both 1H, both dq, *J* = 7.1, *J* = 11.2, 6-NHC<u>H$_a$H$_b$</u>CH$_3$); 3.03 (1H, dd, J_{65b} = 4.1, J_{65a} = 7.5, H-6); 3.96 (1H, dd, J_{5a6} = 7.5, J_{5a5b} = 12.7, H$_a$-5); 4.27 (1H, dd, J_{5b6} = 4.1, J_{5b5a} = 12.7, H$_b$-5); 6.24 (1H, dd, *J* = 2.2, J_{21} = 4.0, H-2); 6.79 (1H, t, *J* = 2.2, H-3); 6.96 (1H, dd, *J* = 2.2, J_{12} = 4.0, H-1). ^{13}C NMR spectrum without proton decoupling, δ, ppm, (*J*, Hz): 15.5 (q, *J* = 125.8, 6-NHCH$_2$<u>CH$_3$</u>); 19.1 (q, *J* = 130.2, 7-(<u>CH$_3$</u>)$_a$); 22.5 (q, *J* = 111.2, 7-(CH$_3$)$_b$); 42.9 (t, *J* = 130.2, 6-<u>CH$_2$</u>CH$_3$); 45.6 (t, *J* = 142.0, C$_{(5)}$); 45.7 (s, C$_{(7)}$); 61.9 (d, *J* = 133.2, C$_{(6)}$); 110.8 (ddd, *J* = 172.7, *J* = 7.3, *J* = 3.6, C$_{(1)}$); 114.4 (ddd, *J* = 174.2, *J* = 7.3, *J* = 4.4, C$_{(2)}$); 125.4 (dm, *J* = 184.4, C$_{(3)}$); 128.7 (m, C$_{(8a)}$); 191.6 (s, C$_{(8)}$). Mass spectrum, *m/z* (I_{rel}, %): 206 [M]$^+$ (12), 163 [M - CH(CH$_3$)$_2$]$^+$ (11), 112 [M - C$_5$H$_3$NO]$^+$ (100). Found, %: C 68.68; H 8.81; N 13.53. C$_{12}$H$_{18}$N$_2$O. Calculated, %: C 68.87; H 8.79; N 13.56.

6-Isopropylamino-7,7-dimethyl-5,6,7,8-tetrahydroindolizinone (3c). IR spectrum, ν, cm^{-1}: 3330 (NH), 1640 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.03, 1.05 (both 3H, both d, *J* = 6.2, 6-NHCH(CH$_3$)$_2$); 1.18, 1.31 (both 3H, both s, 7-(CH$_3$)$_a$, 7-(CH$_3$)$_b$); 2.92 (1H, m, 6-NHC<u>H</u>(CH$_3$)$_2$); 3.08 (1H, dd, J_{65b} = 4.2, J_{65a} = 8.2, H-6); 3.92 (1H, dd, J_{5a6} = 8.2, J_{5a5b} = 12.6, H$_a$-5); 4.28 (1H, dd, J_{5b6} = 4.2, J_{5b5a} = 12.6, H$_b$-5); 6.28 (1H, dd, *J* = 2.3, J_{21} = 4.1, H-2); 6.84 (1H, t, *J* = 2.3, H-3); 7.03 (1H, dd, *J* = 2.3, J_{12} = 4.1, H-1). Mass spectrum, *m/z* (I_{rel}, %): 220 [M]$^+$ (21), 177 [M - CH(CH$_3$)$_2$]$^+$ (12), 126 [M - C$_5$H$_3$NO]$^+$ (100). Found, %: C 70.80; H 9.07; N 12.69. C$_{13}$H$_{20}$N$_2$O. Calculated, %: C 70.90; H 9.09; N 12.72. The reaction of salt **2a** with isopropylamine gave **3c** in 20% yield, **1a** in 12% yield, and **3a** in 3% yield.

3,7,7-Trimethyl-6-methylamino-5,6,7,8-tetrahydroindolizinone (3d). IR spectrum, ν, cm^{-1}: 3350 (NH), 1675 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.18, 1.29 (both 2H, both s, 7-$(CH_3)_a$, 7-$(CH_3)_b$); 2.28 (3H, s, 3-CH_3); 2.51 (3H, s, 6-NH$\underline{CH_3}$); 2.93 (1H, dd, J_{65a} = 6.8, J_{65b} = 3.8, H-6); 3.80 (1H, dd, J_{5a5b} = 13.1, J_{5a6} = 6.8, H_a-5); 4.12 (1H, dd, J_{5b5a} = 13.1, J_{5b6} = 3.8, H_b-5); 6.04 (1H, d, J_{21} = 3.7, H-2); 6.95 (1H, d, J_{12} = 3.7, H-1). Mass spectrum, *m/z* (I_{rel}, %): 206 $[M]^+$ (42), 121 $[M - C(CH_3)_2CHNHCH_3]^+$ (33), 98 $[M - C_6H_5NO]^+$ (100). Found, %: C 69.77; H 8.89; N 13.35. $C_{12}H_{18}N_2O$. Calculated, %: C 69.87; H 8.79; N 13.58.

6-Ethylamino-3,7,7-trimethyl-5,6,7,8-tetrahydroindolizinone (3e). IR spectrum, ν, cm^{-1}: 3340 (NH), 1650 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.12 (3H, t, *J* = 7.1, 6-NHCH$_2\underline{CH_3}$); 1.19, 1.29 (both 3H, both s, 7-$(CH_3)_a$, 7-$(CH_3)_b$); 2.27 (3H, s, 3-CH_3); 2.65, 2.82 (both 1H, both dq, *J* = 7.1, *J* = 10.4, 6-NHC$\underline{H_a}\underline{H_b}CH_3$); 3.03 (1H, dd, J_{65a} = 7.3, J_{65b} = 4.5, H-6); 3.74 (1H, dd, J_{5a6} = 7.3, J_{5a5b} = 12.5, H_a-5); 4.11 (1H, dd, J_{5b6} = 4.5, J_{5b5a} = 12.5, H_b-5); 6.05 (1H, d, J_{21} = 3.9, H-2); 6.95 (1H, d, J_{12} = 3.9, H-1). Mass spectrum, *m/z* (I_{rel}, %): 220 $[M]^+$ (11), 177 $[M - CH(CH_3)_2]^+$ (26), $[M - C_6H_5NO]^+$ (100). Found, %: C 70.80; H 9.25; N 12.79. $C_{13}H_{20}N_2O$. Calculated, %: C 70.87; H 9.15; N 12.72.

6-Methylamino-5,6,7,8-tetrahydrospiro[cyclopentane-1,7'-indolizinone] (3f). IR spectrum, ν, cm^{-1}: 3350 (NH), 1660 C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.59 (1H, m, from 7'-$(CH_2)_4$); 1.72 (4H, m, from 7'-$(CH_2)_4$); 1.94 (2H, m, from 7'-$(CH_2)_4$); 2.33 (1H, m, from 7'-$(CH_2)_4$); 2.44 (3H, s, 6-NH$\underline{CH_3}$); 2.95 (1H, t, *J* = 3.4, H-6); 4.21 (2H, d, *J* = 3.4, 5-CH_2); 6.26 (1H, dd, *J* = 2.2, J_{21} = 4.0, H-2); 6.78 (1H, t, *J* = 2.2, H-3); 6.96 (1H, dd, *J* = 2.2, J_{12} = 4.0, H-1). Mass spectrum, *m/z* (I_{rel}, %): 218 $[M]^+$ (36), 162 $[M - C_4H_8]^+$ (20), 149 $[M - C_5H_9]^+$ (16), 124 $[M - C_5H_3NO]^+$ (100). Found, %: C 69.88; H 8.50; N 8.50. $C_{13}H_{18}N_2O$. Calculated, %: C 71.52; H 8.31; N 12.83.

6-Ethylamino-5,6,7,8-tetrahydrospiro[cyclopentane-1,7'-indolizinone] (3g). IR spectrum, ν, cm^{-1}: 3360 (NH), 1660 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.06 (3H, t, *J* = 7.2, 6-NHCH$_2\underline{CH_3}$); 1.70 (5H, m, from 7'-$(CH_2)_4$); 1.89, 1.98, 2.29 (all 1H, all m, from 7'-$(CH_2)_4$); 2.58, 2.78 (both 1H, both dq, *J* = 7.2, *J* = 11.3, 6-NHC$\underline{H_a}\underline{H_b}CH_3$); 3.16 (1H, t, *J* = 4.1, H-6); 4.12, 4.20 (both 1H, both dd, *J* = 4.1, *J* = 12.9, H_a-5, H_b-5); 6.26 (1H, dd, *J* = 2.2, J_{21} = 4.1, H-2); 6.78 (1H, t, *J* = 2.2, H-3); 6.96 (1H, dd, *J* = 2.2, J_{12} = 4.1, H-1). Mass spectrum, *m/z* (I_{rel}, %): 232 $[M]^+$ (20), 138 $[M - C_5H_3NO]^+$ (100). Found, %: C 72.39; H 8.70; N 11.89. $C_{14}H_{20}N_2O$. Calculated, %: C 72.37; H 8.67; N 12.05.

2,2-Dimethyl-3-methylamino-α-tetralone (6a). IR spectrum, ν, cm^{-1}: 3370 (NH), 1680 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.17, 1.28 (both 3H, both s, 2-$(CH_3)_a$, 2-$(CH_3)_b$); 2.47 (3H, s, 3-NH$\underline{CH_3}$); 2.85 (1H, dd, J_{34b} = 3.7, J_{34a} = 7.2, H-3); 2.90 (1H, dd, J_{4a3} = 7.2, J_{4a4b} = 16.8, H_a-4); 3.24 (1H, dd, J_{4b3} = 3.7, J_{4b4a} = 16.8, H_b-4); 7.23 (1H, d, *J* = 7.8, H-6); 7.30 (1H, t, *J* = 7.8, H-8); 7.46 (1H, dt, *J* = 7.8, J_{79} = 1.2, H-7); 8.02 (1H, dd, *J* = 7.8, J_{97} = 1.2, H-9). Mass spectrum, *m/z* (I_{rel}, %): 203 $[M]^+$ (55), 160 ($[M - CH(CH_3)_2]^+$ (100), 118 $[M - C(CH_3)_2CHNHCH_3]^+$ (33). Found, %: C 76.64; H 8.53; N 6.83. $C_{13}H_{17}NO$. Calculated, %: C 76.81; H 8.43; N 6.89.

3-Ethylamino-2,2-dimethyl-α-tetralone (6b). IR spectrum, ν, cm^{-1}: 3360 (NH), 1670 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.08 (3H, t, *J* = 7.1, 3-NHCH$_2\underline{CH_3}$); 1.16, 1.28 (both 3H, both s, 2-$(CH_3)_a$, 2-$(CH_3)_b$); 2.59, 2.83 (both 1H, both dq, *J* = 7.1, *J* = 11.4, 3-NHC$\underline{H_a}\underline{H_b}CH_3$); 2.90 (1H, dd, J_{4a3} = 7.9, J_{4a4b} = 15.5, H_a-4); 2.95 (1H, dd, J_{34b} = 2.9, J_{34a} = 7.9, H-3); 3.22 (1H, dd, J_{4b3} = 2.9, J_{4b4a} = 15.5, H_b-4); 7.22 (1H, d, *J* = 7.6, H-5); 7.30 (1H, t, *J* = 7.6, H-7); 7.47 (1H, dt, *J* = 7.6, J_{68} = 1.5, H-6); 8.02 (1H, dd, *J* = 7.6, J_{86} = 1.5, H-8). ^{13}C NMR spectrum without proton decoupling, δ, ppm, (*J*, Hz): 15.4 (q, *J* = 125.2, 3-NHCH$_2\underline{CH_3}$); 19.0 (q, *J* = 123.1, 2-($\underline{CH_3}$)$_a$); 22.5 (q, *J* = 127.4, 2-($\underline{CH_3}$)$_b$); 31.6 (t, *J* = 127.8, 3-NH$\underline{CH_2}CH_3$); 42.6 (t, *J* = 129.5, $C_{(4)}$); 47.0 (s, $C_{(2)}$); 62.0 (d, *J* = 131.3, $C_{(3)}$); 126.7 (dd, *J* = 163.2, *J* = 8.0, $C_{(5)}$); 127.8 (dd, *J* = 161.0, *J* = 7.6, $C_{(6)}$); 129.1 (dm, *J* = 157.0, $C_{(7)}$); 131.2 (m, $C_{(4)}$); 133.3 (dd, *J* = 159.6, *J* = 8.8, $C_{(8)}$); 140.3 (m, $C_{(8a)}$); 202.4 (s, $C_{(1)}$). Mass spectrum, *m/z* (I_{rel}, %): 217 $[M]^+$ (100), 174 $[M - CH_2]^+$ (41). Found, %: C 77.45; H 8.42; N 6.52. $C_{14}H_{19}NO$. Calculated, %: C 77.38; H 8.75; N 6.44.

3-Methylaminospiro[cyclohexane-1,2'-α-tetralone] (6d). IR spectrum, ν, cm^{-1}: 3380 (NH), 1680 (C=O). ^{1}H NMR spectrum, δ, ppm, (*J*, Hz): 1.55 (7H, m, from 2'-$(CH_2)_5$); 1.75, 1.84, 2.17 (all 1H, all m, from 2'-$(CH_2)_5$); 2.42 (3H, s, 3-NH$\underline{CH_3}$); 3.10 (1H, dd, J_{4a3} = 2.9, J_{4a4b} = 17.3, H_a-4); 3.18 (1H, t, *J* = 2.9, H-3); 3.25

(1H, dd, J = 2.9, J_{4b4a} = 17.3, H_b-4); 7.23 (1H, d, J = 7.7, H-5); 7.31 (1H, t, J = 7.7, H-7); 7.47 (1H, dt, J_{68} = 1.4, J = 7.7, H-6); 8.00 (1H, dd, J_{86} = 1.4, J = 7.7, H-8). Mass spectrum, *m/z* (I_{rel}, %): 243 $[M]^+$ (34), 160 $[M - C_6H_{11}]^+$ (55), 124 $[M - C_8H_7O]^+$ (100). Found, %: C 78.82; H 8.75; N 5.67. $C_{16}H_{21}NO$. Calculated, %: C 78.97; H 8.69; N 5.75.

3-Isopropylamino-2,2-dimethyl-α-tetralone (6c). IR spectrum, ν, cm^{-1}: 3380 (NH), 1680 (C=O). ^1H NMR spectrum, δ, ppm, (J, Hz): 1.04, 1.06 (both 3H, both d, J = 6.2, 3-NHCH($\underline{CH_3}$)$_a$($\underline{CH_3}$)$_b$); 1.17, 1.31 (both 3H, both s, 2-$(CH_3)_a$, 2-$(CH_3)_b$); 2.93 (3H, m, 3-NHC$\underline{H_a}\underline{H_b}CH_3$); 3.12 (1H, dd, J_{4a3} = 3.0, J_{4a4b} = 16.1, H_a-4); 3.18 (1H, dd, J_{34b} = 3.7, J_{34a} = 3.0, H-3); 3.22 (1H, dd, J_{4b3} = 3.7, J_{4b4a} = 16.1, H_b-4); 7.24 (1H, d, J = 7.7, H-5); 7.32 (1H, t, J = 7.7, H-7); 7.48 (1H, dt, J = 7.7, J_{68} = 1.5, H-6); 8.02 (1H, dd, J = 7.7, J_{86} = 1.5, H-8). Mass spectrum, *m/z* (I_{rel}, %): 231 $[M]^+$ (68), 188 $[M - CH(CH_3)_2]^+$ (25). Found, %: C 77.89; H 9.07; N 6.04. $C_{15}H_{21}NO$. Calculated, %: C 77.92; H 9.09; N 6.06. The yield of the recyclization product **6c** was 25%. The yield of the dealkylation product **4a** was 30%.

REFERENCES

1. A. N. Kost, S. P. Gromov, and R. S. Sagitullin, *Tetrahedron*, **37**, 3423 (1981).
2. C. H. van der Plas, *Tetrahedron*, **41**, 237 (1985).
3. V. I. Terenin, E. V. Kabanova, E. S. Feoktistova, and Yu. G. Bundel', *Khim. Geterotsikl. Soedin.*, 424 (1989).
4. A. N. Kost, V. I. Terenin, L. G. Yudin, R. S. Sagitullin, and A. A. Ivkina, *Khim. Geterotsikl. Soedin.*, 1386 (1979).
5. V. I. Terenin, E. V. Kabanova, and Yu. G. Bundel', *Khim. Geterotsikl. Soedin.*, 763 (1991).
6. W. M. Whaley and T. R. Gvindachari, in: R. Adams, H. Adkins, A. Blate, A. Kopp, F. McGroon, K. Nieman, and G. Snyder (editors), *Organic Reactions* [Russian translation], Izd. Inos. Lit., Vol. 6, Moscow (1953), p. 86.